found that no emergent column correction could be satisfactorily applied ; the pressures, however, under which the saturated solutions boiled were recorded.

The results are given in a tabular form at the end of the paper.

" A Method of Measuring directly High Osmotic Pressures."   By the Earl of BERKELEY and E. G. J. HARTLEY. Communicated by W. C. D. WHETHAM, F.R.S.   Received April 21,—Read June 2, 1904.

This paper gives an account of some preliminary experiments made in furtherance of a scheme of work outlined by one of us in a communication to the Royal Society.*

The ordinary method of determining osmotic pressures, *i.e.*, that adopted by Pfeffer,† Adie,‡ and others, is evidently not suitable for high pressures ; the difficulty of attaching the manometer to the porous pot in a manner such that it will not move at the junction is practically unsurmountable.

It seemed likely that if a porous plate were tightly squeezed between two hollow hemispheres, the necessary conditions of stability might be attained, and the first apparatus carried out this idea. It was made by Messrs. Müller in 1901, and, being of glass, was designed only to stand moderate pressures, though it was hoped that, in a way described below, it might be used to measure indirectly the osmotic pressures of concentrated solutions. It consisted of two glass globes A and B (see fig. 1), holding the porous plate C between them. The plate was glazed round the edge, and carried the semi-permeable membrane of copper ferrocyanide on the face adjacent to the solution. A rubber ring on either side of C and between it and the glass flanges of A and B, served to form a watertight joint when A, B and C were strongly pressed together by means of a suitable brass fitting, which, however, is not shown in the figure.

It had been intended to put solutions of different concentrations in the two vessels, and measure the difference between their osmotic pressures ; it was found that, although it would be possible to obtain the desired result, yet the time taken for the pressure to develop was too long.

An experiment with a solution of 114·7 grammes of sugar in the

* Earl of Berkeley, " Experimental Determinations for Saturated Solutions," read May 19, 1904, see p. 435.
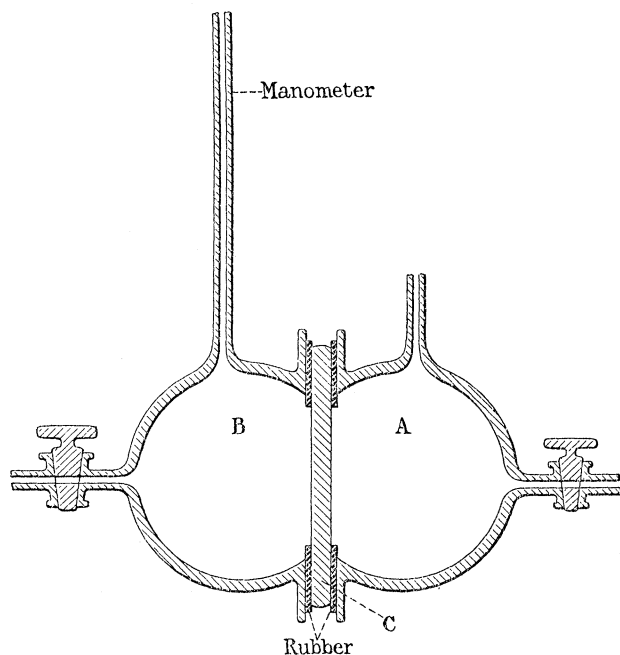
† W. Pfeffer, ' Osmotische Untersuchungen,' Leipsic, 1877.

‡ R. H. Adie, ' Jl. Chem. Soc.,' 1891, p. 344.

litre, gave an osmotic pressure of 8·13 atmospheres, the theoretical value, derived from the gas laws, is 7·89.

This apparatus was discarded, and attempts were made to determine osmotic pressures in a quicker way by a method somewhat similar to that which Tammann[*] tried, *i.e.*, by directly applying to the solution a gradually increasing pressure until the osmotic pressure has been reached, and meanwhile noting the change in the volume of the solvent. We replaced the two glass globes by iron cylinders, and connected one of them, B, which was filled with the solution, to a

Fig. 1.
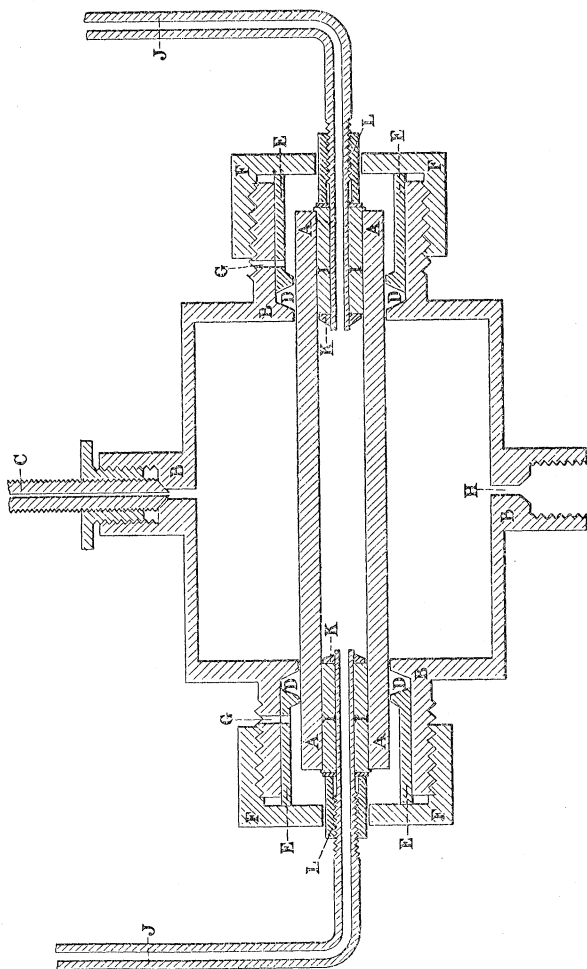
----Manometer

B   A

C

Rubber

powerful pressure apparatus. Water filled the other, A, and also a graduated glass capillary, connected to A by a perforated rubber stopper. Pressure was applied to the solution and the rate at which the water rose in the capillary was noted. The rate was found to be, apparently, slightly different before the osmotic pressure had been reached to that which it was after that pressure had been passed. The phenomenon was so complicated, however, by the volume effect due to the compression of the washers placed on either side of the plate, that no very clear results could be obtained.

* G. Tammann, 'Zeit. f. Phys. Chem.,' vol. 9, p. 97.

Final Form of Apparatus.—We had foreseen this defect, and a means
of overcoming it, should it mask the desired result, was suggested by
Dr. Burton, of the Cambridge Scientific Instrument Company. It con-
sisted in replacing the plate by a porcelain tube; surrounding the

Fig. 2.

middle portion only by the solution and leaving the ends free.   Thus,
when the pressure was applied to the solution, the compression of the
"dermatine" rings, which confine it, would have no effect on the
volume of water inside the tube.

This is embodied in the final form of apparatus which is shown, in
vertical section, in fig. 2.

The porcelain tube, AA, was made of Dr. Puckal's paste by the Royal Berlin Factory, and of a porosity slightly less than that of the porous pots they make for Dr. Thorpe's arsenic apparatus.   It is about 15 c.m. long, and has an outside diameter of 2·5 c.m., and an inside diameter of 1 c.m.   The ends are glazed and the membrane was formed on the whole length of the outer surface.   The outside brass casing BB, contained the solution, to which the pressure was brought by the steel pressure tube C.   The porcelain tube is secured to B by the "dermatine" rings DD, and the latter are strongly compressed, between B and the metal sleeves EE, by screwing down the nuts FF, the lateral expansion causes them to grip the tube tightly.   GG are holes perforated through B, and through the sleeves EE, the use of which will be explained later on.   H is another perforation through B which allows the apparatus to be emptied without taking it to pieces; in several experiments a Schaffer and Budenberg pressure-gauge was attached here, ordinarily it is closed by a screw-down metal plug.

The ends of the porcelain tube are closed by pieces of thick-walled rubber tubing II, through which the brass tubes JJ pass; the length of rubber is such that they extend further into the tube than the distance between the "dermatine" rings and the ends of the tube. A watertight joint between A and J is obtained by compressing the rubber tubes between the metal washers KK, and the screw sleeves LL.   The brass tubes JJ are joined, in one case to a glass tap, and in the other to a glass capillary by rubber tubing.   The glass capillary is graduated in millimetres and was calibrated; 1 cm. of the bore contains ·0042 c.c.

The operation of measuring the osmotic pressure of a solution consisted in filling the inside of the porcelain tube with water, and the surrounding vessel B with the solution; then noting the rate at which the level of the water in the graduated tube moves while the pressure is being gradually increased on the solution.

Theoretically, as long as the osmotic pressure has not been reached, the level of the water in the capillary should fall; when the osmotic pressure is exceeded it should rise and the "turning point" should give the osmotic pressure.   In either case the rate at which it moves is a function of the difference between the osmotic pressure and the pressure on the solution.   In the actual experiments, although the level rose and fell, the "turning point" was at some other pressure higher than the osmotic pressure; the chief cause of this difference was that however tightly the "dermatine" rings were compressed against the porcelain, the sugar solution leaked past them.   This was doubtless because the membrane could not be formed quite on the outer surface of the tube, and consequently a very narrow ring of the tube was left open.   The leak was so small that no difficulty was experienced in keeping the pressure up, even at 50 atmospheres, but

the effect of the leak was gradually to saturate with solution the surface of the exposed portion of the tube, and thus abstract water from the inside through the membrane.

We call this leak the guard-ring leak, and it was hoped that the following method gave us a means of estimating it.

Guard-Ring Leak Correction.—The holes GG (see fig. 2), were bored, and a stream of the solution whose osmotic pressure was to be determined, was directed through them; and to insure that the surface was thoroughly saturated, the whole apparatus was placed in a bath of the same solution. The inside of the tube together with the capillary having been filled with water, and the temperature of the bath and apparatus having become constant, the rate of fall of the level in the capillary was noted. It should be mentioned that the space enclosed by B was also filled with water, and C was replaced by an open glass tube. The level of the water in this open tube was kept at the same height as that in the capillary, so that any small change in the temperature of B did not alter the rate of fall of the level in the capillary.

The guard-ring leak correction was found to be the larger the more concentrated the solution, and it also varied slightly with the height of the water in the capillary.

This correction was of a magnitude such that it *raised* the "turning point," with reference to the pressure, by an amount equal to from 5 to 10 per cent. of the osmotic pressure.

The Solution-Leak Correction.—We have hitherto been unable to make semi-permeable membranes completely impervious to sugar; on testing the water from the inside of the tube a trace was always indicated. It was, therefore, considered advisable to determine the amount of sugar which had come through in each experiment.

At the end of the experiment the inside of the tube was washed out without taking down the apparatus, and its content of sugar analysed by means of Fehling's solution. On the assumption that the resulting quantity of sugar indicated that a corresponding amount of solution had come through the membrane, and on the further assumption that the rate at which this solution came through was proportional both to the time during which it had been subjected to pressure and to the amount of that pressure, the displacement of the "turning point" was calculated.

It was found that, with a good membrane, the solution leak correction was of a magnitude such that it *lowered* the "turning point," with reference to the pressure, by an amount equal to from 2 to 3 per cent. of the osmotic pressure.

In this connection it may be pointed out that a check on the algebraical sum of these two corrections may be obtained from the experiments themselves. For by beginning an experiment at a

pressure on the solution less than its osmotic pressure, and gradually increasing the former until the latter is exceeded, then gradually reducing the pressure until again below the osmotic pressure, the application to the corresponding capillary readings of a formula involving the guard-ring and the solution-leak rates will enable one to calculate the sum of the two.

This sum, deduced in this manner from the capillary readings in an experiment with a solution containing 180 grammes in the litre, was 5·36 cm. The separately determined " guard-ring leak " correction was 10·17 cm., and the difference, 4·81, represents the calculated " solution leak." The observed "solution leak," determined by analysis, and calculated on the assumptions enumerated above, gave 5·03 cm.

Some importance is attached to this method of working as it appears to afford a means of determining the osmotic pressures of solutions of substances for which no truly semi-permeable membranes have yet been found.

The Pressure Apparatus.—The pressure is obtained by means of a vertical steel plunger working in a steel cylinder. The plunger is forced into the cylinder by an iron lever, at one end of which weights are hung, and the bottom of the cylinder is connected with C (see fig. 2). The cylinder and pressure tube are filled with the solution whose osmotic pressure is being determined, and the plunger is made to work almost pressure tight by a " dermatine " ring, sleeve and nut, similar to that shown at D, E and F, in fig. 2. A horizontal lever is attached to the plunger and is worked to and fro, at intervals, so as to keep the pressure on.

The pressure applied when different weights were placed at the end of the lever was determined by connecting the press-tube to a Schaffer and Budenberg standard gauge.

The Formation of the Semi-Permeable Membranes.—Numerous different ways of forming the copper ferrocyanide membrane were tried; the most successful was by first depositing the film by diffusion in the manner Pfeffer* recommends and then finishing it by the electrolytic methods due to Morse and Horn.† The porcelain tubes were immersed in the copper sulphate solution (50 grammes of $CuSO_4,5aq$ in 1000 c.c.) in a desiccator, and exhausted free of air; they were then taken out and their inner and outer surfaces dried with filter paper. The ends were then closed by rubber plugs and they were allowed to dry in the air for from $\frac{1}{2}$ to 1 hour, after which they were quickly plunged into a solution of potassium ferrocyanide (42 grammes in 1000 c.c.). When the membrane was seen to be fairly uniform in colour, the tubes were transferred to the electrolytic cell. This consisted of a beaker containing the ferrocyanide solution in which a platinum foil electrode,

* *Loc. cit.*

† H. N. Morse and D. W. Horn, ' American Chemical Journal,' vol. 26, p. 80.

connected with the negative pole of the battery, was suspended. This electrode was surrounded by a porous pot so as to prevent the solution, when it had been rendered alkaline by the passage of the current, from reaching the membrane on the tube. As mentioned by Morse, we found that the alkaline solution acted injuriously on the membrane. The porcelain tubes were filled with the copper solution, and were furnished with copper electrodes. The voltage used was 100; and when the resistance of the tubes had risen to a constant value, they were taken down and soaked in distilled water for several days. They were then again set up, and the current passed until the resistance was again constant, generally at a higher value than before, upon which they were taken down and washed. This process was repeated till no further change in resistance took place.

The highest resistance obtained was 170,000 ohms ; but out of some fifty tubes only eight or nine reached this figure. These latter were those selected for the experiments, and it was found advisable to re-make the membranes electrolytically after they had been subjected to considerable pressures.

[*May* 21.—We have lately found that the membranes are greatly improved if they be re-made electrolytically under high pressure. The pressure should be applied to a very strong solution of sugar in which the potassium ferrocyanide has been dissolved and which surrounds the outside of the tube ; the inside of the tube being filled with the usual copper sulphate solution and remaining under atmospheric pressure.]

Results.—The following results with cane sugar were obtained ; the experiments were made more for the purpose of testing the method than to get accurate observations of the osmotic pressures ; but we think they are within 10 per cent. of the true values :—

Concentration in grammes per litre.	Pressure at which the "turning point" occurred.	Pressure when "turning point" corrected for guard-ring and solution leaks.	Pressure deduced from Boyle's law.
120 ·7	10 ·5 atmos.	9 ·5 atmos.	8 ·4 atmos.
180 ·0	15 ·7 ,,	14 ·4 ,,	12 ·5 ,,
240 ·0	23 ·6 ,,	21 ·3 ,,	16 ·7 ,,
360 ·0	*	37 ·0 ,,	25 ·1 ,,
420 ·0	45 ·9 ,,	43 ·0 ,,	29 ·2 ,,

Advantages of the Method.—It may be of use briefly to point out what seem to be the advantages of this method :—

* In this experiment the actual "turning point" was not reached.

1. The membrane, owing to the fact that there is no glazed cap to the tube, goes right up to the ends.*

2. There is no necessity to have pressure-tight joints.

3. Greater speed in working ; the actual experiment takes from 2 to 3 hours only.

4. The form of tube used is such that it will withstand very high pressures—it may be of interest to mention that one of the tubes and membrane stood a pressure of 120 atmospheres without apparent harm.

We publish this preliminary notice as it will be some time before the experiments can be continued—a new apparatus has to be cast, and new porcelain tubes are required. We hope, by means of the new apparatus, to reduce greatly the guard-ring leak.

We are glad to avail ourselves of this opportunity to thank Mr. W. C. D. Whetham for the kindly interest he has taken in the research and Mr. H. Darwin for designing the pressure apparatus.

" Colours in Metal Glasses and in Metallic Films." By J. C. MAXWELL GARNETT, B.A., Trinity College, Cambridge. Communicated by Professor LARMOR, Sec. R.S. Received April 19,—Read June 2, 1904.

(Abstract.)

The first part of the paper is devoted to coloured glasses. The phenomena which it seeks to explain were observed by Siedentopf and Zsigmondy.† Expressions are first obtained for the electric vector of the light scattered from a small metal sphere when a train of plane polarised light falls upon it, the investigation following Lord Rayleigh.‡ By means of these expressions it is proved, from the diagrams and statements given by Siedentopf and Zsigmondy, that the metal particles which they observed in gold glass are spherical in shape when the diameters are less than 10^{-5} cm. The fact that such particles are spherical throws light on the manner in which metals crystallise out of solution, the particles taking first a spherical form under the action of surface tension, and later, when they become too large for the forces of surface tension to overcome the crystallic forces, becoming amenable to the latter. Mr. G. T. Beilby has previously arrived at similar conclusions.§

An investigation into the optical properties of a transparent medium

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